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Synthesis of Nitrogen- and Oxygen-Containing Macrocycles with Several Polyamine and Anthracene or Anthraquinone Fragments in Reactions of Palladium-Catalyzed Amination

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Abstract—Palladium-catalyzed amination of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone with polyamines made it possible to synthesize bis(haloaryl)-substituted polyamines and oxadiamines, 1,8-bis-(polyamino)substituted anthracenes and anthraquinones. The dependence of the yield of synthesized main and side products on the reaction conditions and on the nature of initial compounds was investigated. The cyclization of compounds obtained was performed leading to cyclodimers and cyclotrimers, and the limitations of this method were established. A possibility was examined of preparation of N,N-diarylated polyamines derivatives in reactions with excess 1,8-dichloroanthracene or 1,8-dichloroanthraquinone.

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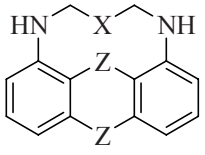
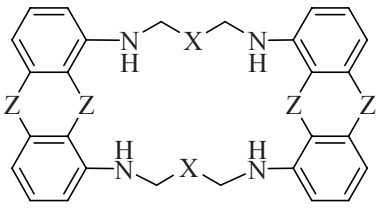
Development of simple and efficient synthetic approaches to compounds including one or several polyamine fragments is an important target of the present-days organic synthesis. One of the approaches consists in the palladium-catalyzed diamination of dihaloarenes with the use of linear polyamines: in this way form compounds with an aryl fragment in a macrocycle. We formerly demonstrated the opportunities of the synthesis of macrocyclic compounds based on 1,2- and 1,3-disunstituted benzene [1], 2,6- and 3,5- disunstituted pyridine [2–4], 1,8- and 1,5-dichloroanthracene and dichloroanthraquinone [5]. In the last decades the aminoanthracenes and aminoanthraquinones are widely employed in the coordination chemistry since their complexes found application as various sensors [6], photo- and redox-switched molecules [7]. These properties of complexes originate from the interaction between the metal ions and the redox-active ligands that results in easy oxidation, reduction [8], and valence tautomerism [9] in these ligands. Ligands of versatile structures were synthesized, among them nitrogen- and oxygen-containing macrocyclic compounds bearing anthracene and anthraquinone substituents. In all formerly synthesized compounds the nitrogen atoms of the macrocycle were linked to the aryl fragment through a methylene group. A special attention was attracted to the synthesis of saturated and tetrapyrrole macrocyclic ligands containing the anthracene or anthraquinone fragments. Compounds with parallel located porphyrin rings connected with a single anthracene bridge proved to be efficient models for the study of photosynthesis [10, 11]. Their bimetallic complexes exhibited a catalytic activity in the reduction of molecular oxygen [12]. Recently an extensive research was directed to saturated bismacrocyclic compounds with a coplanar position of the macrocycles [13]. A general method of synthesis of various compounds of this type was published lately [14]. Crown and azacrown ethers bound to the anthracene or anthraquinone also possess useful properties. For instance, efficient proton sensors were obtained by adding the rings of azacrown ethers to the positions *9* and *10* of anthracene [15]. Diazacrown ethers containing two anthracene fragments are crown-cryptand photoswitches [16, 17]. A molecule containing an anthracene substituent linked to a crown ether was used in detecting Cu^{2+} ions and D-glucosamine [18]. Thus the anthracene and the anthraquinone as fluorophore labels already found a wide application in chemistry.

The goal of this research was the synthesis of molecules containing anthracene and anthraquinone fragments directly linked to the nitrogen atom of the macrocycle. The presence of a bond C(sp^2)–N can significantly affect the coordination of the metal ion by the macrocycle and strengthen the measured response of the aromatic fragment to the complexing. The synthesis of such macrocyclic molecules was considerably limited until recently by the lack of convenient and general methods of building up the C(sp^2)–N bond. For decades the aminoanthraquinones were prepared by Ullmann method involving the catalysis with copper salts [19]. However this method requires stringent conditions and therefore the choice of substrates is limited and the yields are often low. Only relatively recently the first diamino-substituted anthracene was obtained by the nucleophilic substitution in the 1,8-difluoroanthracene [20]. A significant progress was achieved since the middle of nineteen nineties by the synthesis of arylamines through palladium-catalyzed amination of aryl halides [21]. Important investigations were performed with respect to the use of electron-rich ligands, especially for the amination of the less active aryl chlorides [22, 23 The studies of the application of carbene ligands [24] and of the nickel-catalyzed amination of the aryl chlorides [25] also made a significant contribution. Just these studies we used in the synthesis of macrocycles with anthracene and anthraquinone fragments as components of the polyazamacrocycles [5].

Inasmuch as in the reactions of equimolar quantities of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone catalyzed by $Pd(dba)_2$/BINAP and carried out in sufficiently dilute solutions in dioxane (C 0.01–0.03 mol l^{-1}) alongside the polyamines having common macrocycles **A, C, E, F** formed as side products cyclic oligomers **G–J**, whereas in the preparation of macrocycles **B, D** oligomers were absent we performed a special investigation aiming at establishing whether these facts were regular.



A–F



G–J

Z = CH, X = $CH_2O(CH_2)_2OCH_2$ (**A**, **G**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**B**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**C**, **H**); Z = CO, X = $CH_2O(CH_2)_2OCH_2$ (**D**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**E**, **I**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**F**, **J**).

We developed formerly two alternative methods of purposeful synthesis of cyclodimers containing simple aryl fragments (disubstituted benzene and pyridine): through bis(haloaryl) polyamines derivatives and through bis(polyamine) derivatives of arenes [2–4, 26]. In the previous cases the problem was facilitated by the use of aryl bromides, more reactive than aryl chlorides. We tested both approaches in this study. The reaction of 2.2–3.0 equiv of 1,8-dichloroanthracene (**I**) or 1,8-dichloroanthraquinone (**II**) with amines **III–VIII** in more concentrated solutions (0.1–0.2 mol l^{-1}) in the presence of the same catalytic system [$Pd(dba)_2$/BINAP, 4–8 mol%] led to the formation of bis(haloaryl)substituted polyamines **IX–XVII** in 13–53% yield (Scheme 1, *a*, Table 1, runs nos. *1*, *3*, *5–7*, *9*, *11*, *13*, *15*, *18*). In some cases linear oligomers of high molecular weight **XVIII–XXIV** were also isolated by chromatography (Table 1, runs nos. *6*, *11*, *13*). The reduction of the excess of dichloroanthraquinone (**II**) to 1.5 equiv made it possible to isolate oligomer **XXIII** in an acceptable yield (28%, Table 1, run no. *19*), but the similar procedure with dichloroanthracene was inefficient, and the corresponding oligomers **XVIII** and **XIX** were obtained in very low yields (9 and 4% respectively, Table 1, runs nos. *12*, *16*). Once in reaction of dichloroanthraquinone (1.5 equiv) with dioxadiamine **VII** we succeeded in obtaining an even longer oligomer **XXIV** (11%, Table 1, run no. *14*). On the other hand, in reactions of excess 1,8-dichloroanthraquinone with amines **III–V** alongside the desired diarylated derivatives **XII–XIV** formed monoarylated compounds **XXX–XXXII**.

For the synthesis of 1,8-bis(polyamino)substituted anthracene and anthraquinone **XXV–XXIX** 2.5–3-fold excess of amines **III, VI, VIII** was applied (Scheme 1*b*, Table 1, runs nos. *4*, *8*, *10*, *17*, *20*). Yields of the target products was on the average 20–40%, but with the anthraquinone monoamination products **XXX, XXXIII, XXIV** formed in considerable yields (up to 54%).

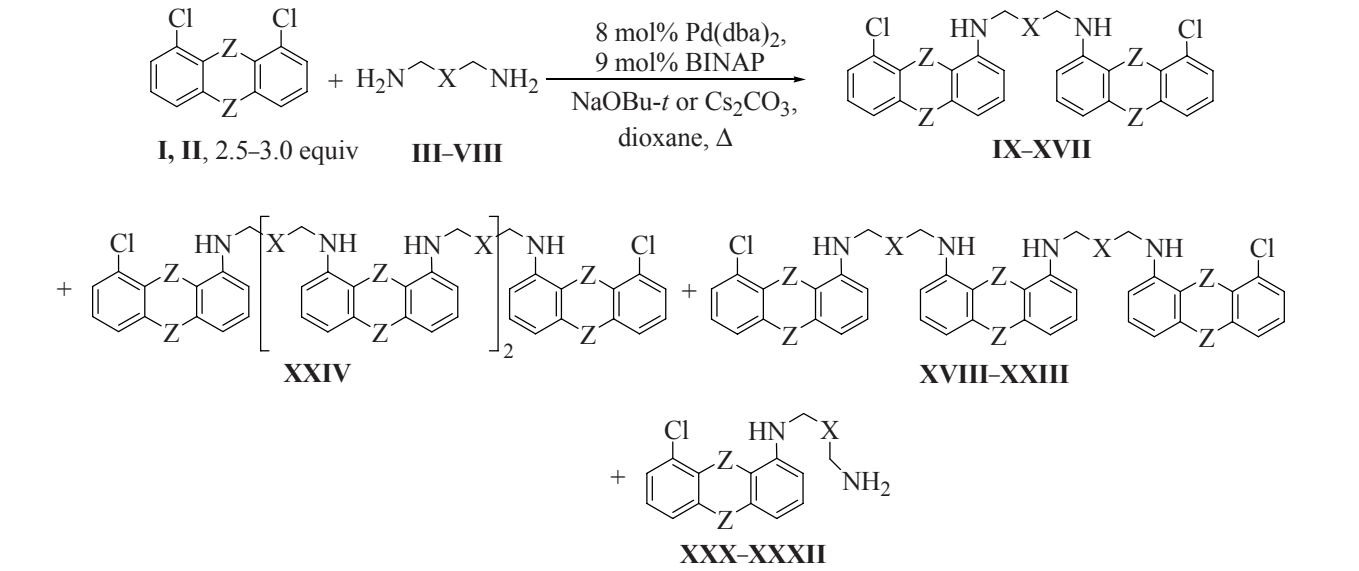
For a purposeful preparation of cyclodimers and cyclotrimers we used reactions of bis(haloaryl)-substituted polyamines with the corresponding aliphatic polyamines (Scheme 2). Reactions of compounds **XII–XIV** with the corresponding amines were inefficient and did not yield the desired cyclodimers. On the contrary, the reaction between dianthryl derivative **IX** and diamine **VI** led to the formation of target cyclic product **XXXV** in 34% yield (Table 2, run no. *1*), the same cyclodimer **G**

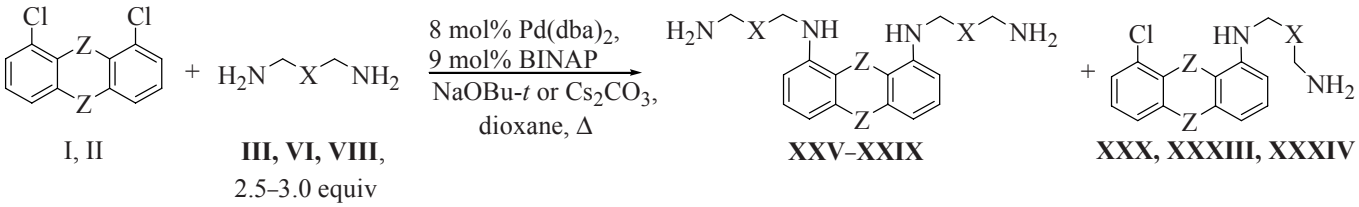
Table 1. Synthesis of bis(haloaryl)-substituted polyamines and linear oligomers **IX–XXIV**, bis(polyamino)-substituted anthracene and anthraquinone **XXV–XXIX**, and mono(polyamino)-substituted anthraquinone derivatives **XXX–XXXIV**

Run no.	Polyamine	Aryl halide	Aryl halide to polyamine ratio	$Pd(dba)_2$–BINAP, mol%	Reagents concentration, mol l^{-1}	Reaction time, h	Reaction products	Yield, % (after chromatography)
1	$NH_2(CH_2)_3NH_2$ (**III**)	**II**	2.2:1	8:9	0.1	15	**XII, XXX**	1154
2	$NH_2(CH_2)_3NH_2$ (**III**)	**II**	1:2.2	8:9	0.1	15	**XXX**	56
3	$NH_2(CH_2)_3NH_2$ (**III**)	**II**	3:1	8:9	0.2	8	**XII, XXX**	2832
4	$NH_2(CH_2)_3NH_2$ (**III**)	**II**	1:3	8:9	0.2	8	**XII, XXVII, XXX**	41661
5	$NH_2(CH_2)_3NH(CH_2)_3NH_2$ (**IV**)	**II**	2.5:1	4:4.5	0.2	8	**XIII, XX, XXXI**	29326
6	$NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (**V**)	**II**	2.5:1	4:4.5	0.2	8	**XIV, XXXII**	136
7	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ (**VI**)	**I**	3:1	4:4.5	0.07	15	**IX**	53
8	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ (**VI**)	**I**	1:2.5	4:4.5	0.2	8	**XXV**	20
9	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ (VI)	**II**	3:1	8:9	0.1	15	**XV, XXI**	389
10	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ (**VI**)	**II**	1:3	8:9	0.1	15	**D**, **XXVIII, XXXIII**	282937
11	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**I**	3:1	4:4.5	0.1	15	**X, XVIII**	4724
12	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**I**	1.8:1	8:9	0.1	15	**X, XVIII**	59
13	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**II**	2.5:1	4:4.5	0.2	8	**E**, **XVI, XXII**	33527
14	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**II**	1.5:1	8:9	0.2	8	**XVI, XXII, XXIV**	301211
15	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**I**	3:1	4:4.5	0.1	15	**XI**	20
16	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**I**	1.8:1	8:9	0.1	15	**XI, XIX**	74
17	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**I**	1:2.5	4:4.5	0.2	8	**XXVI**	40
18	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**II**	3:1	8:9	0.1	15	**F**, **XVII**	629
19	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**II**	1.5:1	8:9	0.2	8	**XVII, XXII**	3628
20	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**II**	1:3	8:9	0.1	15	**F**, **XXIX, XXXIV**	17 20 54

was obtained as impurity in 8% yield in the synthesis of macrocycle **A**. However compound **XV** with the same amine did not form the corresponding cyclodimer **XXXVIII** (Table 2, run no. *2*) in keeping with the total absence of this compound as a side product in the synthesis of macrocycle **D**. A similar situation was observed in the reaction of compounds **X** and **VII**: cyclodimer **XXXVI** was found only in the mass spectrum of

Scheme 1.





Z = CH (**I**), C=O (**II**); X = CH_2 (**III**), $(CH_2)_2NH(CH_2)_2$ (**IV**), $(CH_2)_2NH(CH_2)_2NH(CH_2)_2$ (**V**), $CH_2O(CH_2)_2OCH_2$ (**VI**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**VII**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**VIII**); Z = CH, X = $CH_2O(CH_2)_2OCH_2$ (**IX, XXV**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**X, XVIII**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**XI, XIX, XXVI**); Z = CO, X = CH_2 (**XII, XXVII, XXX**), CH_2NHCH_2 (**XIII, XX, XXXI**), $(CH_2)_2NH(CH_2)_2NH(CH_2)_2$ (**XIV, XXXII**), $CH_2O(CH_2)_2OCH_2$ (**XV, XXI, XXVIII, XXXIII**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**XVI, XXII, XXIV**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**XVII, XXIII, XXIX, XXXIV**).

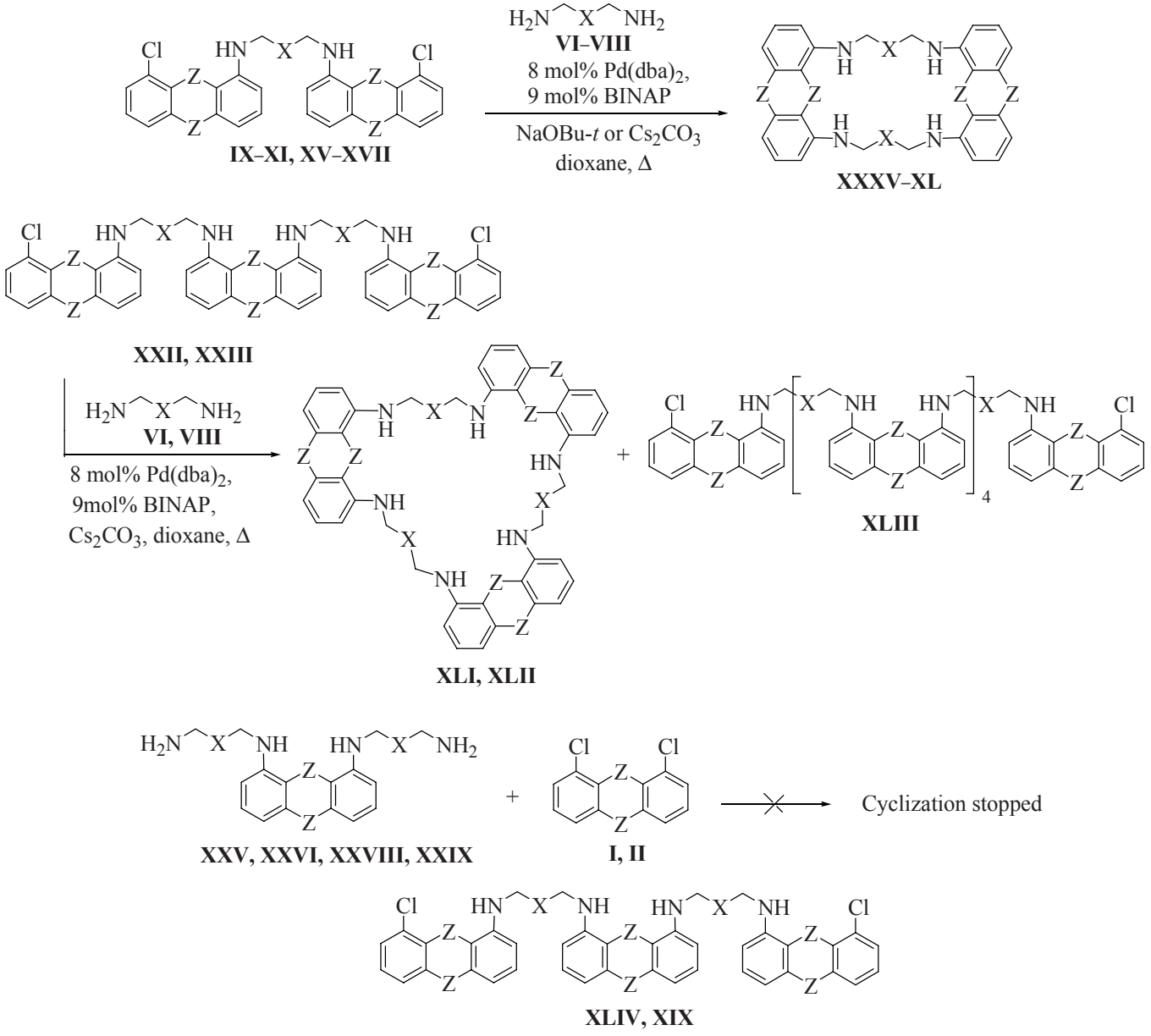
Table 2. Synthesis of cyclooligomers **XXXV–XLII**

Run no.	Polyamine	Haloaryl component	$Pd(dba)_2$–BINAP, mol%	Reagents concentration mol l^{-1}	Reaction time, h	Reaction product	Yield, % (after chromatography)
1	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ (**VI**)	**IX**	8–9	0.027	30	**XXXV**	34
2	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ (**VI**)	**XV**	8–9	0.02	45	**XXXVIII**	0
3	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**X**	8–9	0.02	40	**XXXVI**	traces
4	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**XVI**	8–9	0.02	40	**XXXIX**	21
5	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**XI**	8–9	0.03	30	**XXXVII**	15
6	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**XVII**	8–9	0.03	11	**XL**	37
7	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**XXII**	8–9	0.02	30	**XLI,XLIII**	310
8	$NH_2(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ (**VII**)	**XXII**	8–9	0.01	30	**XLI,XLIII**	520
9	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ (**VIII**)	**XXIII**	8–9	0.02	32	**XLII**	29

the reaction mixture (*m/z* 756.2 $[M]^+$, Table 2, run no. *3*); it also was not isolated as individual side product in the synthesis of macrocycle **B**.

At the same time cyclodimer **XXXIX** was isolated in 21% yield (Table 2, run no. *4*) and also cyclodimers **XXXVII** and **XL**) (yields 15% and 37% respectively, Table 2, run no. *5*, *6*). All these cyclodimers were also obtained in the syntheses of the corresponding macrocycles **C, E**, **F**. Finally, proceeding from linear oligomers **XXII** and **XXIII** we synthesized cyclotrimers **XLI** and **XLII** in 3–5 and 29% yields respectively (Table 2, runs nos. *7–9*) that were also obtained in the course of the synthesis of macrocycles **E**, **F** as side products. The formation of cyclotrimer containing dioxadiamine chains was complicated by the formation of a linear oligomer **XLIII** containing 6 anthraquinone and 5 dioxadiamine

Scheme 2.



Z = CH, X = $CH_2O(CH_2)_2OCH_2$ (**XXXV, XLIV**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**XXXVI**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**XIX, XXXVII**); Z = CO, X = $CH_2O(CH_2)_2OCH_2$ (**XXXVIII**), $(CH_2)_2O(CH_2)_4O(CH_2)_2$ (**XXXIX, XLI, XLIII**), $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ (XL, **XLII**); $(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**XLIV**).

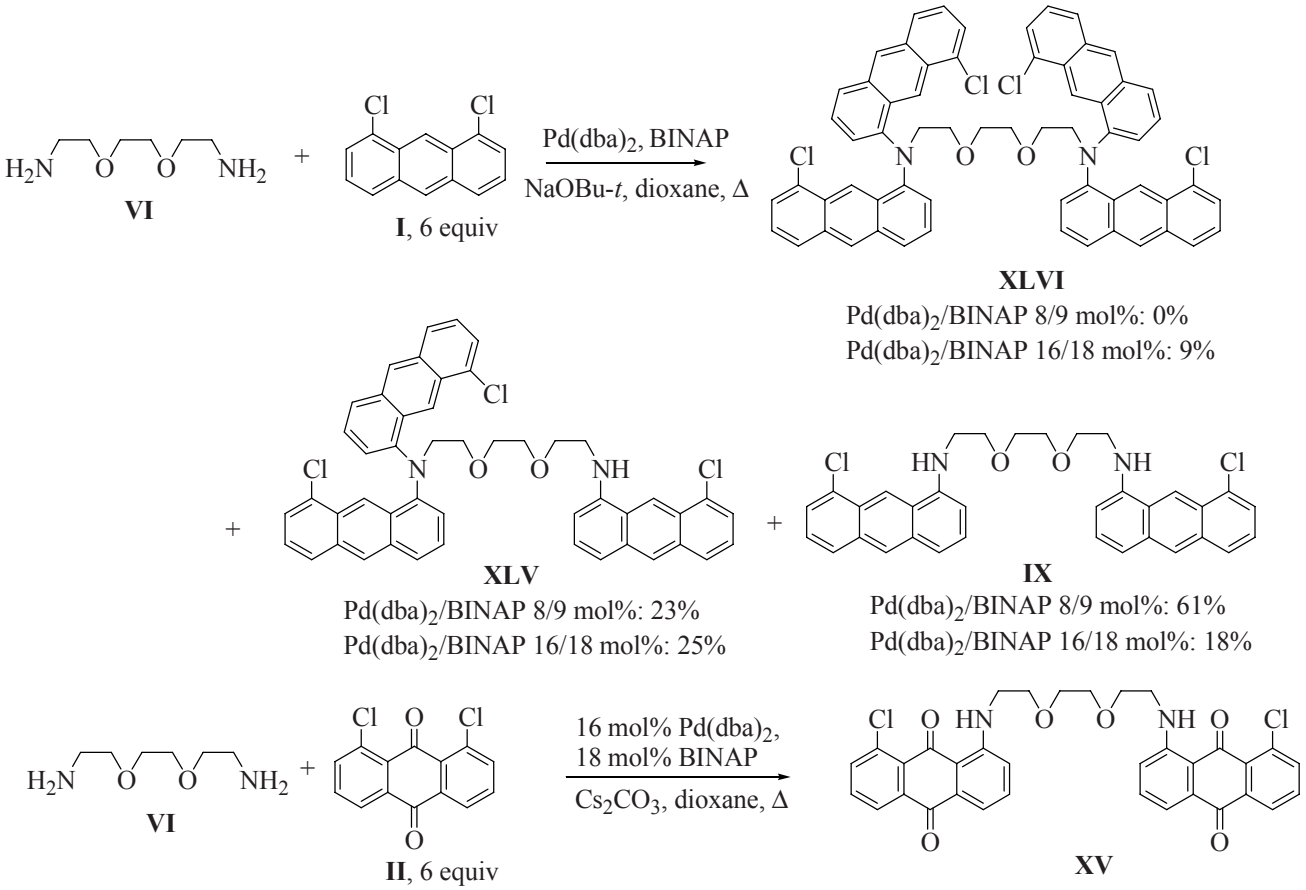
fragments; besides the conversion of the initial compound **XXII** was not sufficiently high, and it was recovered with the yield 29–50%.

The reaction in more diluted solution (*c* 0.01 mol l^{-1}, Table 2, run no. *8*) resulted only in slightly increased yield of the cyclotrimer **XLI**. However even at the standard concentration of reagents (*c* 0.02 mol l^{-1}, Table 2, run no. *9*) cyclotrimer **XLII** was isolated in good yield (29%). Inasmuch as we remarked a complete coincidence between the cyclodimers formation as side products and the possibility of their purposeful synthesis we did not attempt to synthesize cyclotrimers based on anthracene since these compounds were not found among side products in the synthesis of macrocycles **A–C**.

On introducing 1,8-bis(polyamino)-substituted anthracenes and anthraquinones **XXV, XXVI, XXVIII**, and **XXIX** into reactions with compounds **I** or **II** we did not detect even traces of the corresponding cyclodimers (Scheme 2), only at the use of initial **XXVI** and **XXV** were isolated in low yields the corresponding linear oligomers **XIX** and **XLIV** (11 and 20%). This fact is in contrast to the previous results on the use of bis(polyamino) derivatives of pyridine and cholane where at least in some events were successfully synthesized the desired cyclodimers [2–4, 27]. All the mentioned facts suggest that cyclodimers and cyclooligomers arise in the course of amination of 1,8-dichloroanthracene and anthraquinone via intermediate bis(haloaryl) derivatives of polyamines **IX–XVII** or similar linear oligomers **XXII** and **XXIII** but not through bis(polyamino)-substituted anthracenes and anthraquinones **XXV–XXIX**. Moreover, strict limitations exist for the formation of cyclooligomers along the first route, therefore with the same amine anthracene and anthraquinone derivatives might provide different results. It is evidently governed by the preferred geometry of the polyaza(polyoxa) chains, and also by the mutual orientation of two fused aromatic systems.

We found in this study that under the conditions of the synthesis of bis(chloroaryl)-substituted polyamines **IX–XVII** at the use of 2.5–3-fold excess of dichloroanthra-

Scheme 2.



cene or dichloroanthraquinone the products of N,N-diarylation did not form in detectable quantities. On the contrary we had demonstrated previously that products of N,N-diarylation had always formed as impurities in the synthesis of bis(bromophenyl)-substituted polyamines proceeding from *m*-dibromobenzene. Applying sufficient excess of dibromobenzene we were able to synthesize in acceptable yield the tetraarylated derivatives [26]. In this connection it was interesting to study the possibility of N,N-diarylation of polyamines with 1,8-dichloroanthracene and 1,8-dichloroanthraquinone. We chose first dioxadiamine **VI**, whose reaction with 1,8-dichloroanthracene was carried out at the use of a 6-fold excess of the latter in the presence of 8 mol% of catalyst and at the reagents concentration 0.1 mol l^{-1} (Scheme 3).

As a result we obtained triarylated dioxadiamine **XLV** in 23% yield and diarylated amine **IX** in 61% yield, no tetraarylated compound was detected. After increasing the content of the catalyst to 16 mol% tetraarylated derivative **XLVI** was isolated in 9% yield, triarylated amine **XLV**, in 25% yield, and diarylated amine **IX**, in 18% yield. On attempt of polyarylation of triamine **IV** under the same conditions the reaction occurred nonselectively and resulted in intractable mixture of products. At the use in the reaction with dioxadiamine **VI** of 1,8-dichloroanthraquinone (6 equiv) as arylating agent we obtained exclusively diarylated derivative **XV**, and the products of geminal N,N-diarylation were not detected even in traces. These findings indicate that this process occurs with 1,8-dichloroanthracene to a small degree, and is materially impossible with 1,8-dichloroanthraquinone. These results may originate both from the lower activity in the catalityc amination of chlorine compared to bromine and from the greater steric hindrances of anthracene derivatives compared to benzene.

It should be noted in conclusion that all aminoanthraquinones obtained are of red color and have a strong absorption band in the region 500–550 nm. Monoamino-substituted anthraquinones **XII–XVII** are characterized by an absorption band in the region ~520 nm, and in the spectra of diamino-substituted anthraquinones, like cyclodimers or cyclotrimers **XXXIX–XLII** the absorption band shifts to 544 nm, oligomers **XXII–XXIV** containing both mono- and diaminoanthraquinone moieties possess an absorption in an intermediate region (530–540 nm).

Hence a method was developed for the synthesis of cyclodimers containing two at a time aryl and polyamine fragments, and the limits of applicability of this method were demonstrated.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (at operating frequencies 400 and 100.6 MHz respectively) in $CDCl_3$, chloroform signals served for internal reference (δ_H 7.25, δ_C 77.00 ppm). Mass spectra MALDI-TOF of positive ions were measured on an instrument Bruker Daltonics Ultrafex using for matrix 1,8,9-trihydroxyanthracene. The preparative column chromatography was performed using silica gel Merck (40/60).

1,8-Dichloroanthracene (**I**) was synthesized from 1,8-dichloroanthraquinone (**II**) reducing the latter with zinc in ammonia by procedure [28], $Pd(dba)_2$ was synthesized by method [29] and was used without recrystallization. Commercial reagents **II–VIII**, sodium *tert*-butylate, and cesium carbonate were used without additional purification. Dioxane was distilled over alkali and dried by distillation over sodium. Dichloromethane and methanol were purified by distillation.

Bis(haloaryl)-substituted polyamines and oxadiamines IX–XVII, linear oligomers XVIII–XXIV. General procedure. Into a two-neck flask filled with argon and equipped with a reflux condenser and a magnetic stirrer was charged 2.5–3 mmol of 1,8-dichloroanthracene (**I**) (618–741 mg) or of 1,8-dichloroanthraquinonea (**II**) (693–831 mg), 0.04–0.08 mmol (23–46 mg) of $Pd(dba)_2$, 0.045–0.09 mol (28–56 mg) of BINAP, 5–10 ml of anhydrous dioxane, 1 mmol of an appropriate amine **III**–**VIII**, 4 mmol (384 mg) of sodium *tert*-butylate in the case of 1,8-dichloroanthracene or 4 mmol (1352 mg) of cesium carbonate in the case of 1,8-dichloroanthraquinone, and the reaction mixture was heated at reflux for 8–15 h. On completion of boiling the reaction mixture was cooled, the solution was decanted, the precipitate was washed with a little dichloromethane, the combined organic solutions were evaporated in a vacuum, the solid residue was subjected to chromatography on silica gel using the following succession of eluents: CH_2Cl_2, CH_2Cl_2–MeOH, 500:1–3:1, CH_2Cl_2–MeOH–aqueous NH_3, 100:20:1–10:4:1.

***N,N'*-[2,2'-(Ethane-1,2-diylbisoxy)bis(ethane-2,1-diyl)]bis(8-chloroanthracene-1-amine) (IX)** was synthesized from 3 mmol (741 mg) of 1,8-dichloroanthracene (**I**) and 1 mmol (148 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH, 200:1. Yellow-brown crystalline substance, mp 88–90°C. Yield 300 mg (53%). ^{1}H NMR spectrum, δ, ppm: 3.45 t (4H, ^3J 5.3 Hz), 3.82 s (4H), 3.93 t (4H, ^3J 5.2 Hz), 5.06 br.s (2H), 6.35–6.39 m (2H),

7.16–7.21 m (4H), 7.23–7.27 m (2H), 7.43 d.d (2H, ^3J 7.0, ^4J 0.8 Hz), 7.76 d (2H, ^3J 8.5 Hz), 8.14 s (2H), 8.62 s (2H). ^{13}C NMR spectrum, δ, ppm: 43.5 (2C), 69.3 (2C), 70.4 (2C), 102.7 (2C), 115.6 (2C), 117.0 (2C), 124.0 (2C), 124.6 (2C), 124.7 (2C), 124.9 (2C), 126.8 (2C), 126.9 (2C), 127.1 (2C), 127.7 (2C), 131.9 (2C), 132.6 (2C), 143.3 (2C). Mass spectrum MALDI-TOF: *m/z* 568.2 $[M]^+$.

***N,N'*-[3,3'-(Butane-1,4-diylbisoxy)bis(propane-3,1-diyl)]bis(8-chloroanthracene-1-amine) (X)** was synthesized from 1.5 mmol (371 mg) of 1,8-dichloroanthracene (**I**) and 0.5 mmol (102 mg) dioxadiamine **VII**. Eluent CH_2Cl_2–MeOH, 500:1–200:1. Yellow-brown oily substance. Yield 149 mg (47%). ^{1}H NMR spectrum, δ, ppm: 1.69–1.74 m (4H), 2.01 quintet (4H, ^3J 5.8 Hz), 3.35 t (4H, ^3J 6.1 Hz), 3.43–3.47 m (4H), 3.54 t (4H, ^3J 5.5 Hz), 5.37 br.s (2H), 6.47 d (2H, ^3J 6.8 Hz), 7.25–7.39 m (6H), 7.49 d (2H, ^3J 7.2 Hz), 7.82 d (2H, ^3J 8.6 Hz), 8.29 s (2H), 8.72 s (2H). ^{13}C NMR spectrum, δ, ppm: 26.5 (2C), 28.8 (2C), 43.2 (2C), 70.3 (2C), 71.1 (2C), 102.0 (2C), 115.9 (2C), 116.3 (2C), 124.1 (2C), 124.7 (2C), 124.8 (2C), 127.0 (2C), 127.1 (2C), 127.2 (2C), 127.8 (2C), 132.0 (2C), 132.1 (2C), 133.0 (2C), 143.9 (2C). Mass spectrum MALDI-TOF: *m/z* 624.2373 $[M]^+$. $C_{38}H_{38}Cl_2N_2O_2$. Calculated *m/z* 624.2310.

***N,N'*-{3,3'-[2,2'-Oxybis(ethane-2,1-diyl)bisoxy]bis(propane-3,1-diyl)}bis(8-chloroanthracene-1-amine) (XI)** was synthesized from 3 mmol (741 mg) of 1,8-dichloroanthracene (**I**) and 1 mmol (220 mg) of trioxadiamine **VIII**. Eluent CH_2Cl_2. Yellow-brown oily substance. Yield 127 mg (20%). ^{1}H NMR spectrum, δ, ppm: 2.02 quintet (4H, ^3J 5.9 Hz), 3.36 t (4H, ^3J 6.3 Hz), 3.48–3.53 m (4H), 3.58 t (4H, ^3J 5.6 Hz), 3.62–3.67 m (4H), 5.32 br.s (2H), 6.49 d (2H, ^3J 7.1 Hz), 7.28 d.d (2H, ^3J 8.5, ^3J 7.4 Hz), 7.32–7.40 m (4H), 7.50 d (2H, ^3J 7.0 Hz), 7.82 d (2H, ^3J 8.5 Hz), 8.29 s (2H), 8.74 s (2H). ^{13}C NMR spectrum, δ, ppm: 28.6 (2C), 42.7 (2C), 70.1 (2C), 70.3 (2C), 70.5 (2C), 101.9 (2C), 115.8 (2C), 116.2 (2C), 124.0 (2C), 124.6 (2C), 124.7 (2C), 124.9 (2C), 126.9 (2C), 127.0 (2C), 127.2 (2C), 127.6 (2C), 131.9 (2C), 132.8 (2C), 143.8 (2C). Mass spectrum MALDI-TOF: *m/z* 640.2265 $[M]^+$. $C_{38}H_{38}Cl_2N_2O_3$. Calculated *m/z* 640.2259.

8,8'-[Propane-1,3-diylbis(azanediyl)]bis(1-chloroanthracene-9,10-dione) (XII) was synthesized from 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 0.5 mmol (37 mg) of propane-1,3-diamine (**III**). Eluent CH_2Cl_2. Dark-red oily substance. Yield 78 mg (28%). ^{1}H NMR spectrum, δ, ppm: 2.23 quintet (2H, ^3J 6.6 Hz), 3.56 q (4H, ^3J 6.1 Hz), 7.10–7.14 m (2H), 7.50–7.58 m (6H), 7.70 d (2H, ^3J 7.6 Hz), 8.21 d (2H, ^3J 7.3 Hz), 9.71 br.s (2H). ^{13}C NMR spectrum, δ, ppm: 28.6 (1C), 40.8 (2C), 115.1 (2C), 115.4 (2C), 118.1 (2C), 126.4 (2C), 130.6 (2C), 133.7 (2C), 134.5 (2C), 132.7 (2C), 134.9 (2C), 135.2 (2C), 137.9 (2C), 151.3 (2C), 182.9 (2C), 184.2 (2C). Mass spectrum MALDI-TOF: *m/z* 554.2 $[M]^+$.

8,8'-[3,3'-Azanediylbis(propane-3,1-diyl)bis(azanediyl)]bis(1-chloroanthracene-9,10-dione) (XIII) was synthesized from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (131 mg) of triamine **IV**. Eluent–CH_2Cl_2–MeOH, 25:1. Dark-red oily substance. Yield 180 mg (29%). ^{1}H NMR spectrum, δ, ppm: 1.95 quintet (4H, ^3J 6.4 Hz), 2.84 t (4H, ^3J 6.3 Hz), 3.41 q (4H, ^3J 5.8 Hz), 7.04 d (2H, ^3J 7.5 Hz), 7.41–7.46 m (4H), 7.51 t (2H, ^3J 7.8 Hz), 7.69 d (2H, ^3J 8.0 Hz), 8.18 d (2H, ^3J 7.7 Hz), 9.63 br.s (2H) (one proton NH of dialkylamino group cannot be unambiguously assigned). ^{13}C NMR spectrum, δ, ppm: 29.4 (2C), 41.2 (2C), 47.5 (2C), 113.7 (2C), 115.0 (2C), 118.2 (2C), 126.3 (2C), 130.9 (2C), 132.5 (2C). 133.6 (2C), 134.3 (2C), 134.9 (2C), 135.5 (2C), 137.9 (2C), 151.4 (2C), 182.9 (2C), 183.9 (2C). Mass spectrum MALDI-TOF: *m/z* 612.0 $[M + H]^+$.

8,8'-{3,3'-[Ethane-1,2-diylbis(azanediyl)]bis(propane-3,1-diyl)}bis(azanediyl)bis(1-chloroanthracene-9,10-dione) (XIV) was synthesized from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (174 mg) of tetramine **V**. Eluent CH_2Cl_2–MeOH, 5:1–2.5:1. Dark-red oily substance. Yield 87 mg (13%). ^{1}H NMR spectrum, δ, ppm: 2.01 quintet (4H, ^3J 6.7 Hz), 2.94 t (4H, ^3J 6.7 Hz), 3.00 s (4H), 3.37 q (4H, ^3J 6.2 Hz), 6.94–6.99 m (2H), 7.35–7.39 m (4H), 7.49 t (2H, ^3J 7.8 Hz), 7.65 d.d (2H, ^3J 7.9, ^4J 1.4 Hz), 8.11 d.d (2H, ^3J 7.6, ^4J 1.2 Hz), 9.54 t (2H, ^3J 4.7 Hz) (two protons NH of dialkylamino groups cannot be unambiguously assigned). ^{13}C NMR spectrum, δ, ppm: 28.4 (2C), 41.0 (2C), 46.9 (2C), 47.8 (2C), 113.7 (2C), 115.2 (2C), 118.2 (2C), 126.3 (2C), 130.5 (2C), 132.6 (2C), 133.4 (2C), 134.3 (2C), 135.0 (2C), 135.4 (2C), 137.8 (2C), 151.2 (2C), 182.6 (2C), 183.9 (2C). Mass spectrum MALDI-TOF: *m/z* 655.1 $[M + H]^+$.

8,8'-[2,2'-(Ethane-1,2-diylbisoxy)bis(ethane-2,1-diyl)]bis(azanediyl)bis(1-chloroanthracene-9,10-dione) (XV) was synthesized from 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 0.5 mmol (74 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH, 500:1–250:1. Dark-red oily substance. Yield 119 mg (38%). ^{1}H NMR

spectrum, δ, ppm: 3.48 q (4H, ^3J 5.4 Hz), 3.82 s (4H), 3.93 t (4H, ^3J 5.4 Hz), 6.89 d.d (2H, ^3J 8.6, ^4J 1.3 Hz), 7.16 t (2H, ^3J 8.0 Hz), 7.24 d.d (2H, ^3J 7.4, ^4J 1.3 Hz), 7.50 t (2H, ^3J 7.9 Hz), 7.65 d.d (2H, ^3J 7.8, ^4J 1.3 Hz), 8.12 d.d (2H, ^3J 7.9, ^4J 1.3 Hz), 9.71 t (2H, ^3J 5.1 Hz). ^{13}C NMR spectrum, δ, ppm: 42.8 (2C), 69.7 (2C), 72.2 (2C), 113.9 (2C), 115.1 (2C), 118.2 (2C), 126.2 (2C), 130.5 (2C), 132.5 (2C), 133.3 (2C), 134.3 (2C), 134.4 (2C), 135.3 (2C), 137.7 (2C), 151.4 (2C), 182.7 (2C), 183.5 (2C). Mass spectrum MALDI-TOF: *m/z* 628.1195 $[M]^+$. $C_{34}H_{26}Cl_2N_2O_6$. Calculated *m/z* 628.1168.

8,8'-[3,3'-(Butane-1,4-diylbisoxy)bis(propane-3,1-diyl)]bis(azanediyl)bis(1-chloroanthracene-9,10-dione) (XVI) was synthesized from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (202 mg) of dioxadiamine **VII**. Eluent CH_2Cl_2–MeOH, 200:1. Dark-red crystals, mp 182–184°C. Yield 240 mg (35%). At the use of 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (204 mg) of diamine **VII** yield 152 mg (30%). ^{1}H NMR spectrum, δ, ppm: 1.68–1.72 m (4H), 1.98 quintet (4H, ^3J 6.1 Hz), 3.43 t (4H, ^3J 6.1 Hz), 3.46–3.50 m (4H), 3.56 t (4H, ^3J 5.8 Hz), 7.06–7.11 m (2H), 7.44–7.50 m (4H), 7.54 t (2H, ^3J 7.9 Hz), 7.72 d.d (2H, ^3J 7.9, ^4J 1.2 Hz), 8.19 d.d (2H, ^3J 7.7, ^4J 1.2 Hz), 9.64 br.s (2H). ^{13}C NMR spectrum, δ, ppm: 26.5 (2C), 29.4 (2C), 40.2 (2C), 68.1 (2C), 70.9 (2C), 113.8 (2C), 115.0 (2C), 118.3 (2C), 126.3 (2C), 130.8 (2C), 132.5 (2C), 133.6 (2C), 134.4 (2C), 134.9 (2C), 135.5 (2C), 137.9 (2C), 151.6 (2C), 183.0 (2C), 183 (2C). Mass spectrum MALDI-TOF: *m/z* 684.3 $[M]^+$.

8,8'-{3,3'-[2,2'-Oxybis(ethane-2,1-diyl)bisoxy]-bis(propane-3,1-diyl)}bis(azanediyl)bis(1-chloroanthracene-9,10-dione) (XVII) was synthesized from 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 0.5 mmol (110 mg) of trioxadiamine **VIII**. Eluent CH_2Cl_2–MeOH, 250:1. Dark-red crystals, mp 80–82°C. Yield 100 mg (29%). At the use of 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (220 mg) of diamine **VIII** yield 187 mg (36%). UV spectrum, λ_{max}, nm (log ε): 246 (4.92), 280 (4.40), 316 (4.18), 520 (4.08). ^{1}H NMR spectrum, δ, ppm: 1.95 quintet (4H, ^3J 6.4 Hz), 3.36 q (4H, ^3J 6.4 Hz), 3.59 t (4H, ^3J 6.1 Hz), 3.59–3.64 m (4H), 3.67–3.72 m (4H), 6.97–7.02 m (2H), 7.33–7.40 m (4H), 7.47 t (2H, ^3J 7.8 Hz), 7.65 d (2H, ^3J 7.8 Hz), 8.10 d (2H, ^3J 8.2 Hz), 9.55 t (2H, ^3J 5.2 Hz). ^{13}C NMR spectrum, δ, ppm: 29.3 (2C), 40.0 (2C), 68.5 (2C), 70.3 (2C), 70.6 (2C), 113.5 (2C), 114.8 (2C), 118.1 (2C), 126.2 (2C), 130.5 (2C), 132.4 (2C), 133.8 (2C), 134.2 (2C), 134.7 (2C), 135.3 (2C), 137.7 (2C), 151.3 (2C), 182.6 (2C), 183.6 (2C). Mass spectrum MALDI-TOF: *m/z* 700.3 $[M]^+$.

***N*^{1},*N*^{8}-Bis{3-(4-[3-(8-chloroanthracen-1-ylamino)propoxy]butoxy)propyl}anthracene-1,8-diamine (XVIII)** was synthesized from 1.5 mmol (371 mg) of 1,8-dichloroanthracene (**I**) and 0.5 mmol (102 mg) dioxadiamine **VII**. Eluent CH_2Cl_2–MeOH, 100:1. Yellow-brown oily substance. Yield 60 mg (24%). At the use of 1.8 mmol (445 mg) of 1,8-dichloroanthracene (**I**) and 1 mmol (204 mg) of dioxadiamine **VII** yield 45 mg (9%). ^{1}H NMR spectrum, δ, ppm: 1.66 br.s (8H), 1.97 quintet (4H, ^3J 5.5 Hz), 1.98 quintet (4H, ^3J 5.5 Hz), 3.33 t (8H, ^3J 5.9 Hz), 3.39 t (4H, ^3J 5.9 Hz), 3.40 t (4H, ^3J 6.0 Hz), 3.48 t (4H, ^3J 5.7 Hz), 3.49 t (4H, ^3J 5.3 Hz), 5.05 br.s (2H), 5.37 br.s (2H), 6.45 d (2H, ^3J 7.5 Hz), 6.46 d (2H, ^3J 7.5 Hz), 7.26–7.40 m (10H), 7.49 d (2H, ^3J 7.1 Hz), 7.81 d (2H, ^3J 8.3 Hz), 8.25 s (1H), 8.26 s (1H), 8.29 s (2H), 8.73 s (2H). ^{13}C NMR spectrum, δ, ppm: 26.5 (4C), 28.8 (2C), 29.0 (2C), 42.8 (2C), 43.2 (2C), 69.9 (2C), 70.3 (2C), 70.9 (2C), 71.0 (2C), 101.7 (2C), 102.0 (2C), 111.0 (2C), 115.9 (2C), 116.3 (2C), 116.9 (2C), 122.6 (1C), 124.1 (2C), 124.7 (2C), 124.8 (2C), 126.2 (1C), 126.8 (2C), 127.0 (2C), 127.2 (2C), 127.3 (2C), 127.8 (2C), 131.9 (2C), 132.1 (2C), 132.4 (2C), 132.9 (2C), 143.8 (2C), 143.9 (2C). Mass spectrum MALDI-TOF: *m/z* 1002.4592 $[M]^+$. $C_{62}H_{68}Cl_2N_4O_4$. Calculated *m/z* 1002.4618.

***N*^{1},*N*^{8}-Bis{3-[2-(2-[3-(8-chloroanthracen-1-ylamino)propoxy]ethoxy)ethoxy]propyl}-anthracene-1,8-diamine (XIX)** was synthesized from 1.8 mmol (445 mg) of 1,8-dichloroanthracene (**I**) and 1 mmol (220 mg) of trioxadiamine **VIII**. Eluent CH_2Cl_2–MeOH, 100:1. Yellow-brown oily substance. Yield 21 mg (4%). In the synthesis of cyclodimer from 0.4 mmol (245 mg) of compound **XXVI** and 0.4 mmol (99 mg) of 1,8-dichloroanthracene (**I**) yield 44 mg (11%). ^{1}H NMR spectrum, δ, ppm: 1.91 quintet (4H, ^3J 5.8 Hz), 1.97 quintet (4H, ^3J 5.5 Hz), 3.29 t (8H, ^3J 6.2 Hz), 3.34 t (4H, ^3J 6.1 Hz), 3.35 t (4H, ^3J 6.1 Hz), 3.42–3.47 m (8H), 3.57–3.62 m (8H), 5.21 br.s (4H), 6.39–6.46 m (4H), 7.26–7.45 m (10H), 7.49 d (2H, ^3J 7.1 Hz), 7.82 d (2H, ^3J 8.5 Hz), 8.21 s (1H), 8.30 s (2H), 8.31 s (1H), 8.71 s (2H). ^{13}C NMR spectrum, δ, ppm: 28.6 (2C), 28.7 (2C), 42.4 (2C), 42.8 (2C), 70.0 (2C), 70.1 (2C), 70.2 (2C), 70.3 (2C), 70.4 (2C), 70.6 (2C), 101.4 (2C), 102.1 (2C), 118.9 (2C), 115.9 (2C), 116.4 (2C), 116.5 (2C), 122.6 (1C), 124.1 (2C), 124.7 (2C), 124.8 (2C), 126.3 (2C), 126.6 (1C), 127.1 (2C), 127.2 (2C), 127.3 (2C), 127.7 (2C), 132.0 (2C), 132.1 (2C), 132.5 (2C), 133.0 (2C), 143.9

(2C), 144.0 (2C). Mass spectrum MALDI-TOF: *m/z* 1034.4592 $[M]^+$. $C_{62}H_{68}Cl_2N_4O_6$. Calculated *m/z* 1034.4516.

8,8'-{3,3'-[3,3'-(9,10-Dioxo-9,10-dihydroanthracene-1,8-diyl)bis(azanediyl)bis(propane-3,1-diyl)]bis(azanediyl)bis(propane-3,1-diyl)}bis-(azanediyl)bis(1-chloroanthracene-9,10-dione) (XX) was obtained as a side product in the synthesis of compound **XIII** from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (131 mg) of triamine **IV**. Eluent CH_2Cl_2–MeOH–aqueous NH_3, 100:20:3. Dark-red oily substance. Yield 15 mg (3%). UV spectrum, λ_{max}, nm (log ε): 282 (4.19), 316 (3.99), 506 (3.97). ^{1}H NMR spectrum, δ, ppm: 1.96 t (8H, ^3J 6.1 Hz), 2.86 t (8H, ^3J 6.4 Hz), 3.32–3.40 m (8H), 6.90 d (2H, ^3J 8.5 Hz), 6.98 d.d (2H, ^3J 7.9, ^4J 1.1 Hz), 7.32 t (2H, ^3J 7.9 Hz), 7.37–7.45 m (6H), 7.49 t (2H, ^3J 7.9 Hz), 7.67 d.d (2H, ^3J 7.7, ^4J 1.2 Hz), 8.15 d.d (2H, ^3J 7.9, ^4J 1.2 Hz), 9.59 br.s (4H). Mass spectrum MALDI-TOF: *m/z* 947.2 $[M + H]^+$.

8,8'-[2,2'-{2,2'-[2,2'-(9,10-Dioxo-9,10-dihydroanthracene-1,8-diyl)bis(azanediyl)bis-(ethane-2,1-diyl)]bisoxybis(ethane-2,1-diyl)}bis(oxy)bis(ethane-2,1-diyl)]bis(azanediyl)bis(1-chloroanthracene-9,10-dione) (XXI) was obtained as a side product in the synthesis of compound **XV** from 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 0.5 mmol (74 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH, 100:1. Dark-red oily substance. Yield 23 mg (9%). ^{1}H NMR spectrum, δ, ppm: 3.40 q (4H, ^3J 5.4 Hz), 3.41 q (4H, ^3J 5.3 Hz), 3.77 s (8H), 3.83 t (8H, ^3J 5.5 Hz), 6.81 d.d (2H, ^3J 8.0, ^3J 1.0 Hz), 6.86 d (2H, ^3J 8.6 Hz), 7.16 t (2H, ^3J 8.0 Hz), 7.30 d.d (2H, ^3J 7.4, ^3J 1.2 Hz), 7.39–7.40 (4H), 7.46 t (2H, ^3J 7.9 Hz), 7.62 d.d (2H, ^3J 7.8, ^3J 1.5 Hz), 8.09 d.d (2H, ^3J 7.6, ^3J 1.5 Hz), 9.56 t (2H, ^3J 5.2 Hz), 9.65 t (2H, ^3J 4.8 Hz). ^{13}C NMR spectrum, δ, ppm: 42.6 (2C), 42.8 (2C), 69.5 (2C), 69.8 (2C), 70.9 (2C), 71.0 (2C), 113.8 (2C), 114.4 (2C), 114.8 (2C), 115.0 (2C), 117.3 (2C), 117.9 (2C), 126.3 (2C), 130.5 (4C), 132.4 (4C), 133.3 (2C), 134.3 (2C), 134.6 (2C), 135.4 (2C), 137.7 (2C), 150.8 (2C), 151.2 (2C), 182.5 (2C), 183.0 (1C), 183.5 (2C), 183.9 (1C). Mass spectrum MALDI-TOF: *m/z* 980.2 $[M]^+$.

8,8'-[3,3'-{4,4'-[3,3'-(9,10-Dioxo-9,10-dihydroanthracene-1,8-diyl)bis(azanediyl)bis-(propane-3,1-diyl)]bisoxybis(butane-4,1-diyl)}-bisoxybis(propane-3,1-diyl)]bis(azanediyl)bis-(1-chloroanthracene-9,10-dione) (XXII) was obtained as a side product in the synthesis of compound **XVI** from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (202 mg) of diamine **VII**. Eluent CH_2Cl_2–MeOH, 100:1. Dark-red oily substance. Yield 146 mg (27%). At the use of 1.5 mmol (416 mg) of 1,8-dichloro-anthraquinone (**II**) and 1 mmol (204 mg) of dioxadiamine **VII** yield 66 mg (12%). ^{1}H NMR spectrum, δ, ppm: 1.65–1.72 m (8H), 1.95 quintet (8H, ^3J 6.2 Hz), 3.56 q (4H, ^3J 6.3 Hz), 3.58 q (4H, ^3J 6.3 Hz), 3.44–3.48 m (8H), 3.53 t (4H, ^3J 5.8 Hz), 3.55 t (4H, ^3J 5.9 Hz), 6.96 d.d (2H, ^3J 8.5, ^3J 1.1 Hz), 7.01–7.04 m (2H), 7.38 t (2H, ^3J 7.9 Hz), 7.41–7.45 m (6H), 7.50 t (2H, ^3J 7.9 Hz), 7.68 d.d (2H, ^3J 8.0, ^3J 1.5 Hz), 8.16 d.d (2H, ^3J 7.7, ^3J 1.4 Hz), 9.55 t (2H, ^3J 5.0 Hz), 9.60 br.s (2H). ^{13}C NMR spectrum, δ, ppm: 26.5 (4C), 29.4 (2C), 29.5 (2C), 40.1 (2C), 40.2 (2C), 68.1 (2C), 68.2 (2C), 70.9 (4C), 113.7 (2C), 114.3 (2C), 114.8 (2C), 114.9 (2C), 117.5 (2C), 118.2 (2C), 126.5 (2C), 130.6 (2C), 132.4 (2C), 133.5 (2C), 134.0 (2C), 134.2 (2C), 134.4 (2C), 134.8 (2C), 135.5 (2C), 137.8 (2C), 151.1 (2C), 151.5 (2C), 182.9 (2C), 183.8 (2C), 184.4 (1C), 188.8 (1C). Mass spectrum MALDI-TOF: *m/z* 1093.3 $[M + H]^+$.

1-Chloro-8-(3-{3-[2-(3-{8-[3-(2-{2-[3-(8-chloro-9,10-dioxo-9,10-dihydroanthracen-1-ylamino)propoxy]ethoxy}ethoxy)propylamineO]-9,10-dioxo-9,10-dihydroanthracen-1-ylamino}propoxy)-ethoxy]propoxy}propylamino)anthracene-9,10-dione (XXIII) was synthesized from 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (220 mg) of trioxadiamine **VIII**. Eluent CH_2Cl_2–MeOH, 100:1. Dark-red oily substance. Yield 156 mg (28%). ^{1}H NMR spectrum, δ, ppm: 1.95 quintet (8H, ^3J 5.7 Hz), 3.30 q (4H, ^3J 5.8 Hz), 3.35 q (4H, ^3J 5.9 Hz), 3.60 (8H, ^3J 6.3 Hz), 3.56–3.64 m (8H), 3.65–3.70 m (8H), 6.90 d (2H, ^3J 8.3 Hz), 6.97–7.01 m (2H), 7.33 t (2H, ^3J 7.9 Hz), 7.35–7.41 m (6H), 7.46 t (2H, ^3J 7.6 Hz), 7.64 d (2H, ^3J 7.8 Hz), 8.11 d (2H, ^3J 7.7 Hz), 9.45 br.s (2H), 9.55 br.s (2H). ^{13}C NMR spectrum, δ, ppm: 29.3 (2C), 29.4 (2C), 39.9 (2C), 40.0 (2C), 68.5 (2C), 68.6 (2C), 70.3 (4C), 70.6 (4C), 113.5 (2C), 114.1 (2C), 114.7 (2C), 114.9 (2C), 117.4 (2C), 118.1 (2C), 126.2 (2C), 130.5 (2C), 132.4 (2C), 133.4 (2C), 133.9 (2C), 134.1 (2C), 134.3 (2C), 134.8 (2C), 135.3 (2C), 137.7 (2C), 151.0 (2C), 151. 4 (2C), 182.7 (2C), 183.6 (2C), 184.2 (1C), 188.56 (1C). Mass spectrum MALDI-TOF: *m/z* 1124.7 $[M]^+$.

8,8'-[3,3'-{4,4'-[3,3'-{8,8'-[3,3'-(Butane-1,4-diyl-bisoxy)bis(propane-3,1-diyl)]bis(azanediyl)bis(9,10-dioxo-9,10-dihydroanthracene-8,1-diyl)}bis-(azanediyl)bis(propane-3,1-diyl)]bis(oxy)bis(butane-

4,1-diyl)}bisoxybis(propane-3,1-diyl)]bis(azanediyl)-bis(1-chloroanthracene-9,10-dione) (XXIV) was obtained as a side product in the synthesis of compound **XVI** from 1.5 mmol (416 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (204 mg) of dioxadiamine **VII**. Eluent CH_2Cl_2–MeOH, 100:1. Dark-red oily substance. Yield 55 mg (11%). UV spectrum, λ_{max}, nm (log ε): 250 (4.91), 286 (4.49), 316 (4.28), 534 (4.34). ^{1}H NMR spectrum, δ, ppm: 1.68 br.s (12H), 1.96 quintet (12H, ^3J 5.4 Hz), 3.36 q (8H, ^3J 6.8 Hz), 3.39 q (4H, ^3J 6.4 Hz), 3.46 br.s (12H), 3.51–3.57 m (12H), 6.96 d (4H, ^3J 8.5 Hz), 7.02–7.07 m (2H), 7.38 t (4H, ^3J 7.8 Hz), 7.42–7.48 m (8H), 7.51 t (2H, ^3J 7.8 Hz), 7.69 d (2H, ^3J 7.9 Hz), 8.17 d (2H, ^3J 7.7 Hz), 9.55 t (4H, ^3J 4.7 Hz), 9.62 br.s (2H). ^{13}C NMR spectrum, δ, ppm: 26.5 (6C), 29.4 (2C), 29.6 (4C), 40.1 (4C), 40.2 (2C), 68.1 (2C), 68.2 (4C), 70.9 (6C), 113.8 (2C), 114.4 (4C), 114.8 (4C), 115.0 (2C), 117.6 (4C), 118.2 (2C), 126.3 (2C), 130.7 (2C), 132.5 (2C), 133.6 (2C), 134.0 (4C), 134.3 (4C), 134.4 (2C), 134.9 (2C), 135.5 (2C), 137.9 (2C), 151.2 (4C), 151.5 (2C), 182.9 (2C), 183.9 (2C), 184.5 (2C), 188.9 (2C). Mass spectrum MALDI-TOF: *m/z* 1500.8 $[M]^+$.

Bis(polyamino)-substituted anthracenes and anthraquinones XXV–XXIX, mono(polyamino)-substituted anthraquinones XXX–XXXIV. *General procedure.* Into a two-neck flask filled with argon and equipped with a reflux condenser and magnetic stirrer was charged 1 mmol of 1,8-dichloroanthracene (**I**) (247 mg) or 1,8-dichloroanthraquinone (**II**) (277 mg), 0.04–0.08 mmol (23–46 mg) of $Pd(dba)_2$, 0.045–0.09 mol (28–56 mg) of BINAP, 5–10 ml of anhydrous dioxane, 2.5–3 mmol of an appropriate amine **III, VI**, or **VIII**, 4 mmol (384 mg) of sodium *tert*-butylate in the case of 1,8-dichloroanthracene or 4 mmol (1352 mg) of cesium carbonate in the case of 1,8-dichloroanthraquinone, and the reaction mixture was heated at reflux for 8–15 h. On completion of boiling the reaction mixture was cooled, the solution was decanted, the precipitate was washed with a little dichloromethane, the combined organic solutions were evaporated in a vacuum, the solid residue was subjected to chromatography on silica gel using the following succession of eluents: CH_2Cl_2, CH_2Cl_2–MeOH, 500:1–3:1; CH_2Cl_2–MeOH–aqueous NH_3, 100:20:1–10:4:1.

***N*^{1},*N*^{8}-Bis{2-[2-(2-aminoethoxy)ethoxy]ethyl}-anthracene-1,8-diamine (XXV)** was synthesized from 1 mmol (247 mg) of 1,8-dichloroanthracene (**I**) and 2.5 mmol (370 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH, 2.5:1. Yellow oily substance. Yield 94 mg (20%). ^{1}H NMR spectrum, δ, ppm: 2.75 t (4H, ^3J 4.8 Hz), 3.37 t (4H, ^3J 5.0 Hz), 3.49–3.58 m (8H), 3.60–3.65 m (4H), 3.87 t (4H, ^3J 4.8 Hz), 6.36–6.44 m (2H), 7.22–7.30 m (4H), 8.19 s (1H), 8.92 C (1H) (signals of NH protons cannot be unambiguously assigned). ^{13}C NMR spectrum, δ, ppm: 40.7 (2C), 43.7 (2C), 68.9 (2C), 69.5 (2C), 69.7 (2C), 70.9 (2C), 101.0 (2C), 113.5 (2C), 116.6 (2C), 122.7 (1C), 126.2 (2C), 126.3 (1C), 132.5 (2C), 144.0 (2C). Mass spectrum MALDI-TOF: *m/z* 470.4 $[M]^+$.

***N*^{1},*N*^{8}-Bis(3-{2-[2-(3-aminopropoxy)ethoxy]-ethoxy}propyl)anthracene-1,8-diamine (XXVI)** was synthesized from 1 mmol (247 mg) of 1,8-dichloroanthracene (**I**) and 2.5 mmol (550 mg) of trioxadiamine **VIII**. Eluent – CH_2Cl_2–MeOH–aqueous NH_3, 100:20:3. Yellow oily substance. Yield 245 mg (40%). ^{1}H NMR spectrum, δ, ppm: 1.54 quintet (4H, ^3J 6.4 Hz), 2.07 quintet (4H, ^3J 6.1 Hz), 2.65 t (4H, ^3J 6.7 Hz), 3.31 t (4H, ^3J 6.1 Hz), 3.34–3.69 m (24H), 6.42–6.46 m (2H), 7.25–7.30 m (4H), 8.20 s (1H), 8.57 s (1H) (signals of NH protons cannot be unambiguously assigned). ^{13}C NMR spectrum, δ, ppm: 28.6 (2C), 32.2 (2C), 39.3 (2C), 41.9 (2C), 69.2 (2C), 69.7 (2C), 69.9 (2C), 70.0 (2C), 70.2 (2C), 70.3 (2C), 101.0 (2C), 112.4 (2C), 116.2 (2C), 122.5 (1C), 126.3 (2C), 126.4 (1C), 132.4 (2C), 144.1 (2C). Mass spectrum MALDI-TOF: *m/z* 614.3 $[M]^+$.

1,8-Bis(3-aminopropylamino)anthracene-9,10-dione (XXVII) was synthesized from 0.5 mmol (139 mg) of 1,8-dichloroanthraquinone (**II**) and 1.5 mmol (111 mg) of propane-1,3-diamine (**III**). Eluent CH_2Cl_2–MeOH–aqueous NH_3, 100:20:3. Dark-red oily substance. Yield 28 mg (16%). ^{1}H NMR spectrum, δ, ppm: 1.90 quintet (4H, ^3J 6.9 Hz), 2.90 t (4H, ^3J 6.9 Hz), 3.37 q (4H, ^3J 6.3 Hz), 7.00 d (2H, ^3J 8.6 Hz), 7.44 t (2H, ^3J 8.0 Hz), 7.51 d (2H, ^3J 7.3 Hz), 9.58 t (2H, ^3J 4.1 Hz) (proton signals of primary amino groups cannot be unambiguously assigned). ^{13}C NMR spectrum, δ, ppm: 32.9 (2C), 40.0 (2C), 40.6 (2C), 144.4 (2C), 114.9 (2C), 117.6 (2C), 134.1 (2C), 134.3 (2C), 151.1 (2C), 184.6 (1C), 189.0 (1C). Mass spectrum MALDI-TOF: *m/z* 353.1 $[M + H]^+$.

1,8-Bis{2-[2-(2-aminoethoxy)ethoxy]ethyl-amino}anthracene-9,10-dione (XXVIII) was synthesized from 0.5 mmol (139 mg) of 1,8-dichloroanthraquinone (**II**) and 1.5 mmol (222 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH–aqueous NH_3, 100:20:2. Dark-red oily substance. Yield 71 mg (29%). ^{1}H NMR spectrum, δ, ppm: 2.03 br.s (4H), 2.92 t (4H, ^3J 4.8 Hz), 3.46–3.52 m (8H), 3.62–3.69 m (8H), 3.76 t (4H, ^3J 5.7 Hz), 6.99 d (2H, ^3J 8.4 Hz), 7.41 t (2H, ^3J 8.0 Hz),

7.49 d.d (2H, ^3J 7.3, ^4J 1.2 Hz), 9.67 t (2H, ^3J 5.2 Hz). ^{13}C NMR spectrum, δ, ppm: 41.6 (2C), 42.6 (2C), 69.5 (2C), 70.2 (2C), 70.5 (2C), 73.2 (2C), 114.6 (2C), 115.0 (2C), 117.5 (2C), 134.0 (2C), 134.3 (2C), 151.0 (2C), 184.4 (1C), 188.8 (1C). Mass spectrum MALDI-TOF: *m/z* 501.2 $[M + H]^+$.

1,8-Bis(3-{2-[2-(3-aminopropoxy)ethoxy]-ethoxy}propylamino)anthracene-9,10-dione (XXIX) was synthesized from 0.5 mmol (139 mg) of 1,8-dichloroanthraquinone (**II**) and 1.5 mmol (330 mg) of trioxadi-amine **VIII**. Eluent–CH_2Cl_2–MeOH, 3:1. Dark-red oily substance. Yield 84 mg (20%). ^{1}H NMR spectrum, δ, ppm: 1.68 quintet (4H, ^3J 5.8 Hz), 1.96 quintet (4H, ^3J 6.4 Hz), 2.74 t (4H, ^3J 7.0 Hz), 3.35 q (4H, ^3J 6.3 Hz), 3.45–3.67 m (24H), 4.05 br.s (4H), 6.98 d (2H, ^3J 8.4 Hz), 7.39 t (2H, ^3J 7.7 Hz), 7.45 d (2H, ^3J 7.4 Hz), 9.55 t (2H, ^3J 5.2 Hz). ^{13}C NMR spectrum, δ, ppm: 29.3 (2C), 32.5 (2C), 39.2 (2C), 39.9 (2C), 68.6 (2C), 69.2 (2C), 70.0 (2C), 70.2 (4C), 70.5 (2C), 114.2 (2C), 114.7 (2C), 117.6 (2C), 134.0 (2C), 134.1 (2C), 151.1 (2C), 182.9 (1C), 184.5 (1C). Mass spectrum MALDI-TOF: *m/z* 645.3 $[M + H]^+$.

1-(3-Aminopropylamino)-8-chloroanthracene-9,10-dione (XXX) was obtained as the main product from 0.5 mmol (139 mg) of 1,8-dichloroanthraquinone (**II**) and 1.5 mmol (111 mg) of propane-1,3-diamine (**III**). Eluent CH_2Cl_2–MeOH, 5:1–2.5:1. Red oily substance. Yield 96 mg (61%). ^{1}H NMR spectrum, δ, ppm: 1.50 br.s (2H), 1.89 quintet (2H, ^3J 6.7 Hz), 2.89 t (2H, ^3J 6.9 Hz), 3.39 q (2H, ^3J 6.3 Hz), 7.04–7.09 m (1H), 7.45–7.50 m (2H), 7.54 t (1H, ^3J 7.8 Hz), 7.72 d.d (1H, ^3J 7.9, ^4J 1.2 Hz), 8.20 d.d (1H, ^3J 7.7, ^4J 1.2 Hz), 9.59 br.s (1H). ^{13}C NMR spectrum, δ, ppm: 32.7, 39.8, 40.6, 113.8, 115.0, 118.2, 126.3, 130.7, 132.6, 133.6, 134.4, 135.0, 135.5, 137.9, 151.5, 183.0, 184.0. Mass spectrum MALDI-TOF: *m/z* 314.9 $[M + H]^+$.

1-[3-(3-Amine propylamine)propylamine]-8-chloroanthracene-9,10-dione (XXXI) was obtained as a side product in the synthesis of compound XIII from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (131 mg) of triamine **IV**. Eluent CH_2Cl_2–MeOH–aqueous NH_3, 100:20:3. Red oily substance. Yield 98 mg (26%). ^{1}H NMR spectrum, δ, ppm: 1.64 quintet (2H, ^3J 6.9 Hz), 1.69 br.s (3H), 1.91 quintet (2H, ^3J 6.8 Hz), 2.69 t (2H, ^3J 6.9 Hz), 2.77 t (4H, ^3J 6.8 Hz), 3.38 q (2H, ^3J 6.4 Hz), 7.03–7.08 m (1H), 7.44–7.50 m (2H), 7.53 t (1H, ^3J 7.9 Hz), 7.71 d (1H, ^3J 7.0 Hz), 8.19 d (1H, ^3J 6.8 Hz), 9.60 t (1H, ^3J 4.4 Hz). ^{13}C NMR spectrum, δ, ppm: 29.5, 33.4, 40.6, 41.1, 47.5, 48.0, 113.7, 115.0, 118.3, 126.3, 130.7, 132.5, 133.6, 134.4, 134.9, 135.5, 137.9, 151.5, 182.9, 184.0. Mass spectrum MALDI-TOF: *m/z* 372.2 $[M + H]^+$.

1-{3-[2-(3-Aminopropylamino)ethylamino]-propylamino}-8-chloroanthracene-9,10-dione (XXXII) was obtained as a side product in the synthesis of compound **XIV** from 2.5 mmol (693 mg) of 1,8-dichloroanthraquinone (**II**) and 1 mmol (174 mg) tetramine **V**. Eluent–CH_2Cl_2–MeOH–aqueous NH_3, 10:3:1. Red oily substance. Yield 25 mg (6%). ^{1}H NMR spectrum, δ, ppm: 1.65 quintet (2H, ^3J 6.6 Hz), 1.91 quintet (2H, ^3J 6.5 Hz), 2.72 t (2H, ^3J 7.0 Hz), 2.76 s (4H), 2.76–2.82 m (4H), 2.85 br.s (4H), 3.37 q (2H, ^3J 6.2 Hz), 7.03–7.07 m (1H), 7.44–7.49 m (2H), 7.53 t (1H, ^3J 7.7 Hz), 7.70 d (1H, ^3J 7.6 Hz), 8.17 d (1H, ^3J 7.6 Hz), 9.58 t (1H, ^3J 4.5 Hz). ^{13}C NMR spectrum, δ, ppm: 29.3, 32.0, 40.6, 41.0, 47.3, 48.0, 48.9, 49.0, 113.7, 115.0, 118.3, 126.3, 130.7, 132.5, 133.5, 134.3, 134.9, 135.4, 137.9, 151.4, 182.9, 183.9. Mass spectrum MALDI-TOF: *m/z* 415.3 $[M + H]^+$.

1-{2-[2-(2-Aminoethoxy)ethoxy]ethylamino}-8-chloroanthracene-9,10-dione (XXXIII) was obtained as a side product in the synthesis of compound **XXVIII** from 0.5 mmol (139 mg) of 1,8-dichloroanthraquinone (**II**) and 1.5 mmol (222 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH, 10:1. Red oily substance. Yield 72 mg (37%). ^{1}H NMR spectrum, δ, ppm: 2.42 br.s (2H), 2.85 t (2H, ^3J 5.2 Hz), 3.52 q (2H, ^3J 5.5 Hz), 3.53 t (2H, ^3J 5.3 Hz), 3.64–3.71 m (4H), 3.79 t (2H, ^3J 5.8 Hz), 7.06–7.11 m (1H), 7.46–7.51 m (2H), 7.54 t (1H, ^3J 7.8), 7.72 d.d (1H, ^3J 7.8, ^4J 1.4 Hz), 8.20 d.d (1H, ^3J 7.6, ^4J 1.4 Hz), 9.69 t (1H, J 4.9 Hz). ^{13}C NMR spectrum, δ, ppm: 41.7, 42.8, 69.5, 70.3, 70.7, 73.3, 114.1, 115.2, 118.2, 126.3, 130.7, 132.6, 133.6, 134.5, 134.9, 135.5, 137.9, 151.4, 183.0, 184.0. Mass spectrum MALDI-TOF: *m/z* 388.0 $[M]^+$.

1-(3-{2-[2-(3-Aminopropoxy)ethoxy]ethoxy}propylamino)-8-chloroanthracene-9,10-dione (XXXIV) was obtained as a side product in the synthesis of compound **XXIX** from 0.5 mmol (139 mg) of 1,8-dichloroanthraquinone (**II**) and 1.5 mmol (330 mg) of trioxadiamine **VIII**. Eluent–CH_2Cl_2–MeOH, 10:1. Red oily substance. Yield 124 mg (54%). ^{1}H NMR spectrum, δ, ppm: 1.71 quintet (2H, ^3J 6.4 Hz), 1.97 quintet (2H, ^3J 6.3 Hz), 2.63 br.s (2H), 2.78 t (2H, ^3J 6.4 Hz), 3.40 q (2H, ^3J 6.4 Hz), 3.51 t (2H, ^3J 6.0 Hz), 3.52–3.67 m (10H), 7.02–7.07 m (1H), 7.42–7.45 m (2H), 7.50 t (1H, ^3J 7.9 Hz), 7.67 d.d (1H, ^3J 7.9, ^4J 1.0 Hz), 8.14 d.d (1H, ^3J 8.0, ^4J 1.0 Hz), 9.58 t (1H, ^3J 5.3 Hz). ^{13}C NMR spectrum, δ, ppm: 29.2, 32.3, 39.4, 40.0, 68.6, 69.4, 70.0,

70.3, 70.4 (2C), 113.6, 114.9, 118.2, 126.2, 130.6, 132.4, 133.4, 134.3, 134.8, 135.4, 137.8, 151.4, 182.8, 183.8. Mass spectrum MALDI-TOF: *m/z* 461.3 $[M + H]^+$.

Cyclodimers and cyclotrimers XXXV–XLII. *General procedure.* Into a two-neck flask filled with argon and equipped with a reflux condenser and a magnetic stirrer was charged 0.5 mmol of bis(haloaryl) derivative of polyamine **IX–XVII** or of linear oligomer **XXII–XXIII**, 0.04 mmol (23 mg) of $Pd(dba)_2$, 0.045 mol (28 mg) of BINAP, 17–50 ml of anhydrous dioxane, 0.5 mmol of an appropriate amine **VI–VIII**, 2 mmol (192 mg) of sodium *tert*-butylate in the case of 1,8-dichloroanthracene or 2 mmol (676 mg) of cesium carbonate in the case of 1,8-dichloroanthraquinone, and the reaction mixture was heated at reflux for 11–45 h. On completion of boiling the reaction mixture was cooled, the solution was decanted, the precipitate was washed with a little dichloromethane, the combined organic solutions were evaporated in a vacuum, the solid residue was subjected to chromatography on silica gel using the following succession of eluents: CH_2Cl_2, CH_2Cl_2–MeOH, 500:1–3:1; CH_2Cl_2–MeOH–aqueous NH_3, 100:20:1–10:4:1.

11,12,14,15,18,19,30,31,33,34,37,38-Dodecahydro-10*H*,17*H*,29*H*,36*H*-4,6:25,23-dimetheno-tetrabenzo[*h*,*k*,*w*,*z*]-[1,4,16,19,7,13,22,28]tetraoxatetraazacyclotriacontine (XXXV) [5] was synthesized from 0.35 mmol (200 mg) of compound **IX** and 0.35 mmol (52 mg) of dioxadiamine **VI**. Eluent CH_2Cl_2–MeOH, 100:1. Yellow crystalline substance, mp 88–90°C. Yield 77 mg (34%). ^{1}H NMR spectrum, δ, ppm: 3.45 t (8H, ^3J 5.0 Hz), 3.77 s (8H), 3.91 t (8H, ^3J 5.0 Hz), 5.43 br.s (4H), 6.37 d (4H, ^3J 7.3 Hz), 7.26 t (4H, ^3J 8.0 Hz), 7.33 d (4H, ^3J 8.2 Hz), 8.24 C (2H), 8.60 C (2H). Mass spectrum MALDI-TOF: *m/z* 644.1 $[M]^+$.

10,11,12,13,15,16,18,19,21,22,23,24,-34,35,36,37,39,40,42,43,45,46,47,48-Tetracosahydro-4,6:30,28-dimethenotetrabenzo[*l*,*o*,*f*$_1$,*i*$_1$][1,4,7,21,24,27,11,17,31,37]hexaoxatetraazacyclotetracontine (XXXVII) [5] was synthesized from 0.2 mmol (140 mg) of compound **XI** and 0.2 mmol (44 mg) of trioxadiamine **VIII**. Eluent– CH_2Cl_2. Yellow oily substance. Yield 23 mg (15%). ^{1}H NMR spectrum, δ, ppm: 1.98 quintet (8H, ^3J 6.2 Hz), 3.37 t (8H, ^3J 6.3 Hz), 3.51 t (8H, ^3J 5.7 Hz), 3.50–3.58 m (8H), 3.64–3.72 m (8H), 5.50 br.s (4H), 6.39–6.43 m (4H), 7.25–7.32 m (8H), 8.20 s (2H), 8.44 s (2H). ^{13}C NMR spectrum, δ, ppm: 29.0 (4C), 42.9 (4C), 70.5 (4C), 70.6 (8C), 101.8 (4C), 112.4 (4C), 117.0 (4C), 123.1 (2C), 126.8 (4C), 127.1 (2C), 132.9 (4C), 144.5 (4C). Mass spectrum MALDI-TOF: *m/z* 788.1 $[M]^+$.

10,11,12,13,15,16,17,18,20,21,22,23,33,34,35,-36,38,39,40,41,43,45,46-Tricosahydro-5*H*,28*H*-4,6:27,29-dimethanotetrabenzo[*f*,*i*,*y*,*b*$_1$]-[1,15,20,34,5,11,24,30]-tetraoxatetraazacyclooctatriacontine-5,28,47,48-tetrone (XXXIX) [5] was synthesized from 0.11 mmol (76 mg) of compound **XVI** and 0.11 mmol (22 mg) of dioxaamine **VII**. Eluent CH_2Cl_2–MeOH, 200:1. Dark-red crystalline substance, mp 230–232°C. Yield 19 mg (21%). UV spectrum, λ_{max}, nm (log ε): 250 (4.45), 282 (4.29), 544 (4.18). ^{1}H NMR spectrum, δ, ppm: 1.72 br.s (8H), 1.98 quintet (8H, ^3J 6.2 Hz), 3.40 q (8H, ^3J 5.6 Hz), 3.50 br.s (8H), 3.57 t (8H, ^3J 5.6 Hz), 6.98 d (4H, ^3J 8.1 Hz), 7.42 t (4H, ^3J 7.8 Hz), 7.49 d (4H, ^3J 7.1 Hz), 9.66 br.s (4H). ^{13}C NMR spectrum, δ, ppm: 26.5 (4C), 29.1 (4C), 40.1 (4C), 68.3 (4C), 70.9 (4C), 114.5 (4C), 114.8 (4C), 117.5 (4C), 134.0 (4C), 134.4 (4C), 151.1 (4C), 184.6 (2C), 188.9 (2C). Mass spectrum MALDI-TOF: *m/z* 816.7 $[M]^+$.

10,11,12,13,15,16,18,19,21,22,23,24,34,35,36,-37,39,40,42,43,45,46,47,48-Tetracosahydro-5*H*,29*H*-4,6:28,30-dimethanotetrabenzo[*l*,*o*,*f*$_1$,*i*$_1$]-[1,4,7,21,24,27,11,17,31,37]hexaoxatetraazacyclotetracontine-5,29,49,50-tetrone (XL) [5] was synthesized from 0.14 mmol (100 mg) of compound **XVII** and 0.14 mmol (31 mg) of trioxadiamine **VIII**. Eluent CH_2Cl_2–MeOH, 100:1. Dark-red crystalline substance, mp 195–197°C. Yield 44 mg (37%). UV spectrum, λ_{max}, nm (lge): 282 (4.31), 306 (4.00), 544 (4.25). ^{1}H NMR spectrum, δ, ppm: 1.97 quintet (8H, ^3J 6.5 Hz), 3.32 q (8H, ^3J 6.3 Hz), 3.62 t (8H, ^3J 6.3 Hz), 3.63–3.66 m (8H), 3.68–3.72 m (8H), 6.88 d.d (4H, ^3J 8.4, ^4J 1.3 Hz), 7.34 t (4H, ^3J 7.7 Hz), 7.40 d.d (4H, ^3J 7.2, ^4J 1.3 Hz), 9.55 t (4H, ^3J 5.2 Hz). ^{13}C NMR spectrum, δ, ppm: 29.7 (4C), 40.5 (4C), 69.2 (4C), 70.8 (4C), 71.1 (4C), 114.7 (4C), 115.2 (4C), 117.8 (4C), 134.3 (4C), 134.6 (4C), 151.4 (4C), 184.8 (2C), 188.9 (2C). Mass spectrum MALDI-TOF: *m/z* 848.1 $[M]^+$.

Cyclotrimer XLI was synthesized from 0.06 mmol (70 mg) of compound **XXII** and 0.06 mmol (13 mg) of dioxadiamine **VII**. Eluent–CH_2Cl_2–MeOH, 100:1. Dark-red crystalline substance. Yield 4 mg (5%). ^{1}H NMR spectrum, δ, ppm: 1.68 br.s (12H), 1.95 quintet (12H, ^3J 5.9 Hz), 3.34 q (12H, ^3J 5.8 Hz), 3.46 br.s (12H), 3.53 t (12H, ^3J 5.4 Hz), 6.94 d (6H, ^3J 8.6 Hz), 7.38 t (6H, ^3J 7.8 Hz), 7.45 d (6H, ^3J 7.3 Hz), 9.54 t (6H, ^3J 4.5 Hz). ^{13}C NMR spectrum, δ, ppm: 26.5 (6C), 29.4 (6C), 40.1 (6C), 68.2 (6C), 70.8 (6C), 114.3 (6C), 114.8

(6C), 117.5 (6C), 134.0 (6C), 134.2 (6C), 151.0 (6C), 184.4 (3C), 188.8 (3C). Mass spectrum MALDI-TOF: *m/z* 1224.7 $[M]^+$.

Cyclotrimer XLII was synthesized from 0.096 mmol (110 mg) of compound **XXIII** and 0.096 mmol (21 mg) of trioxadiamine **VIII**. Eluent–CH_2Cl_2–MeOH, 100:1. Dark-red crystalline substance. Yield 36 mg (29%). UV spectrum, λ_{max}, nm (log ε): 280 (4.37), 316 (4.07), 544 (4.27). ^{1}H NMR spectrum, δ, ppm: 1.94 quintet (12H, ^3J 6.4 Hz), 3.30 q (12H, ^3J 6.3 Hz), 3.60 t (12H, ^3J 6.1 Hz), 3.61–3.65 m (12H), 3.66–3.70 m (12H), 6.90 d (6H, ^3J 8.4 Hz), 7.34 t (6H, ^3J 7.9 Hz), 7.41 d (6H, ^3J 7.2 Hz), 9.46 t (6H, ^3J 4.7 Hz). ^{13}C NMR spectrum, δ, ppm: 29.4 (6C), 40.0 (6C), 68.7 (6C), 70.4 (6C), 70.7 (6C), 114.3 (6C), 114.7 (6C), 117.5 (6C), 133.9 (6C), 134.2 (6C), 151.0 (6C), 184.3 (3C), 188.7 (3C). Mass spectrum MALDI-TOF: *m/z* 1273.3 $[M + H]^+$.

Oligomer XLIII was obtained as a second product in the synthesis of compound **XLI**. Dark-red oily substance. Yield 14 mg (20%). UV spectrum, λ_{max}, nm (log ε): 280 (4.77), 318 (4.52), 542 (4.69). ^{1}H NMR spectrum, δ, ppm: 1.68 br.s (20H), 1.95 quintet (20H, ^3J 5.9 Hz), 3.34 q (20H, ^3J 5.8 Hz), 3.46 br.s (20H), 3.53 t (20H, ^3J 5.4 Hz), 6.94 d (8H, ^3J 8.6 Hz), 7.01–7.06 m (2H), 7.38 t (8H, ^3J 7.8 Hz), 7.42–7.47 m (12H), 7.50 t (2H, ^3J 7.9 Hz), 7.68 d.d (2H, ^3J 8.0, ^4J 1.4 Hz), 8.16 d.d (2H, ^3J 7.7, ^4J 1.4 Hz), 9.57 t (8H, ^3J 5.1 Hz), 9.61 br.s (2H). ^{13}C NMR spectrum, δ, ppm: 26.5 (10C), 29.5 (8C), 29.7 (2C), 40.1 (10C), 68.1 (2C), 68.2 (8C), 70.8 (10C), 114.3 (8C), 114.8 (8C), 115.0 (2C), 117.5 (8C), 118.2 (2C), 126.3 (2C), 132.5 (2C), 134.0 (8C), 134.2 (8C), 134.9 (2C), 137.9 (2C), 151.1 (8C), 184.4 (4C), 188.8 (4C) (quaternary carbon atoms of aminochloroanthraquinone fragments were not determined). Mass spectrum MALDI-TOF: *m/z* 2316.9950 $[M]^+$. $C_{134}H_{146}Cl_2N_{10}O_{22}$. Calculated *m/z* 2316.9990.

***N*^{1},*N*^{8}-Bis(2-{2-[2-(8-chloroanthracen-1-ylamino)ethoxy]ethoxy}ethyl)anthracene-1,8-diamine (XLIV)** was obtained in the attempted synthesis of cyclodimer from 0.2 mmol (94 mg) of compound **XXV** and 0.2 mmol (49 mg) of 1,8-dichloroanthracene (**I**). Eluent CH_2Cl_2–MeOH, 250:1. Yellow-brown oily substance. Yield 35 mg (20%). ^{1}H NMR spectrum, δ, ppm: 3.37 t (4H, ^3J 5.0 Hz), 3.41 t (4H, ^3J 5.1 Hz), 3.73 s (8H), 3.83 t (4H, ^3J 5.0 Hz), 3.85 t (4H, ^3J 5.1 Hz), 5.04 br.s (4H), 6.31 d (2H, ^3J 7.7 Hz), 6.33 d (2H, ^3J 8.1 Hz), 7.14 t (2H, ^3J 7.8 Hz), 7.20–7.35 m (8H), 7.43 d (2H, ^3J 7.1 Hz), 7.77 d (2H, ^3J 8.4 Hz), 8.07 s (1H), 8.21 s (2H), 8.25 s (1H), 8.66 s (2H). ^{13}C NMR spectrum, δ, ppm: 43.6 (2C), 43.7 (2C), 69.2 (2C), 69.5 (2C), 70.2 (2C), 70.4 (2C), 102.1 (2C), 102.7 (2C), 111.2 (2C), 115.7 (2C), 117.2 (2C), 117.3 (2C), 122.6 (1C), 124.1 (2C), 124.7 (2C), 124.9 (2C), 125.9 (2C), 126.4 (1C), 126.9 (2C), 127.1 (2C), 127.2 (2C), 127.6 (2C), 131.9 (2C), 132.0 (2C), 132.2 (2C), 132.8 (2C), 143.2 (2C), 143.3 (2C). Mass spectrum MALDI-TOF: *m/z* 890.2 $[M]^+$.

8-Chloro-*N*-(8-chloroanthracene-1-yl)-*N*-(2-{2-[2-(8-chloroanthracen-1-ylamino)ethoxy]ethoxy}-ethyl)anthracene-1-amine (XLV) was synthesized by the procedure described for compound **IX** from 3 mmol (741 mg) of 1,8-dichloroanthracene (**I**), 0.5 mmol (74 mg) of dioxadiamine **VI**, 23 mg (16 mol%) of $Pd(dba)_2$, 28 mg (18 mol%) of BINAP, 2.5 mmol (260 mg) of sodium *tert*-butylate, 5 ml of anhydrous dioxane (boiling for 14 h). Eluent petroleum ether–CH_2Cl_2, 1:2. Yellow-brown oily substance. Yield 96 mg (25%). UV spectrum, λ_{max}, nm (log ε): 370 (4.17), 400 (4.20). ^{1}H NMR spectrum, δ, ppm: 3.29 t (2H, ^3J 5.2 Hz), 3.68–3.75 m (4H), 3.77 t (2H, ^3J 5.2 Hz), 4.11 t (2H, ^3J 6.3 Hz), 4.19 t (2H, ^3J 6.3 Hz), 5.01 br.s (1H), 6.40 d (1H, ^3J 6.7 Hz), 7.17–7.37 m (11H), 7.44 d (1H, ^3J 7.2 Hz), 7.64 d (2H, ^3J 8.2 Hz), 7.78 d (2H, ^3J 8.2 Hz), 7.80 d (1H, ^3J 8.3 Hz), 8.28 s (1H), 8.31 s (2H), 8.67 s (1H), 9.48 s (2H). ^{13}C NMR spectrum, δ, ppm: 43.5 (1C), 53.6 (1C), 69.0 (1C). 69.2 (1C), 70.4 (1C), 71.0 (1C), 102.7 (1C), 115.9 (1C), 117.0 (1C), 119.4 (2C), 120.5 (2C), 124.1 (2C), 124.6 (1C), 124.7 (1C), 124.8 (1C), 124.9 (2C), 125.1 (2C), 125.2 (1C), 125.7 (2C), 127.0 (4C), 127.1 (3C), 127.8 (1C), 128.8 (2C), 129.0 (2C), 132.0 (1C), 132.2 (2C), 132.4 (2C), 132.8 (1C), 133.5 (2C), 143.5 (1C), 147.3 (2C). Mass spectrum MALDI-TOF: *m/z* 778.3 $[M]^+$.

***N*,*N*'-[2,2'-(Ethane-1,2-diylbisoxy)bis(ethane-2,1-diyl)]bis[8-chloro-N-(8-chloroanthracen-1-yl)anthracene-1-amine] (XLVI)** was obtained as a second product in the synthesis of compound **XLV**. Yellow-brown oily substance. Yield 46 mg (9%). ^{1}H NMR spectrum, δ, ppm: 3.58 s (4H), 3.92 t (4H, ^3J 6.5 Hz), 4.04 t (4H, ^3J 6.5 Hz), 7.16 d (4H, ^3J 7.2 Hz), 7.23 t (4H, ^3J 7.4 Hz), 7.27 t (4H, ^3J 7.8 Hz), 7.35 d (4H, ^3J 7.1 Hz), 7.67 d (4H, ^3J 8.3 Hz), 7.79 d (4H, ^3J 8.4 Hz), 8.33 s (4H), 9.40 s (4H). ^{13}C NMR spectrum, δ, ppm: 53.5 (2C), 68.9 (2C), 70.8 (2C), 119.4 (4C), 120.6 (4C), 124.1 (4C), 125.0 (4C), 125.1 (4C), 125.8 (4C), 127.0 (4C), 127.1 (4C), 128.9 (4C), 129.1 (4C), 132.2 (4C), 132.5 (4C), 133.6 (4C), 147.4 (4C). Mass spectrum MALDI-TOF: *m/z* 988.4 $[M]^+$.

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